Synthesis and Characterizations of CCTO Ceramics by Solid State Reaction Route

A Thesis submitted for the partial fulfillment of the Degree of M.Sc. in Physics

by

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CERTIFICATE

This is to certify that the dissertation entitled "**Synthesis and Characterizations of CCTO Ceramic by Solid State Reaction Route**" which is being submitted by **Miss Supriya Chandra**, M.Sc. student of Department of Physics, National Institute of Technology, Rourkela in partial fulfillment of the requirements for the degree of M.Sc. in Physics is a record of independent research work done by her under my guidance.

The matter incorporated in the thesis has not been submitted to any other University/Institute for the award of any degree.

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Supriya Chandra

ABSTRACT

$CaCu_3Ti_4O_{12}$ (CCTO) ceramics were synthesized by solid state reaction route. Calcination temperature was optimized. The sample was calcined for 1000^0C for 4, 8 and 12hours. Single perovskite phase was confirmed from XRD analysis for the samples calcined for 12hours. CCTO ceramics were conventionally sintered at 1050ºC for 4, 6, and 8hrs, respectively. Density measurements, XRD analysis, dielectric constant and dielectric loss measurements, SEM and P-E hysteresis loop studies were done. Highest density was achieved in sample conventionally sintered for 6 hrs. Dielectric measurements were done in the frequency range 1 kHz to 1 MHz. Electrical properties such as dielectric constant and dielectric loss were studied as a function of temperature and frequency, which showed a diffused phase transition.

CONTENT

CHAPTER 1

1.1 INTRODUCTION

1.1.1 Insulators

An electrical insulator is a material whose internal electric charges do not flow freely, and due to which it does not conduct an electric current, by applying electric field. An insulator which is perfect does not exist in nature, but some materials such as glass, paper etc having higher resistivity are very good electrical insulators. A larger class of materials not having higher bulk resistivity are also good enough to insulate electrical wirings and cables. Some of the examples are rubber-like polymers and most plastics. Almost all insulators have large band gap because of the "valence" band consisting of the highest energy electrons is full, and the next band is separated from it by a large energy gap above it. There is always some voltage named as breakdown voltage that will give the electrons enough energy to be excited into this band. Once the voltage i.e. the breakdown voltage is exceeded the material discontinue being an insulator, and charge starts passing through it. Insulators are commonly used as a flexible coating on electric wire and cable which prevents a dangerous electrical shock when we touch the wire.

1.1.2 Dielectrics

A dielectric is an electrical insulator that can be polarized only by applying an applied electric field [1]. Whenever a dielectric is placed in an electric field, electric charges stops flowing through the material but slight shift from their average equilibrium positions causes dielectric polarization. The term dielectric is used to indicate the energy storing capacity of the material .An example of a dielectric is placing a ceramic material between the metallic

plates of a capacitor. If the voltage across a dielectric material becomes too great or if the electrostatic field becomes too strong the material will suddenly begin to conduct current. This process is called dielectric breakdown .

An important property of a dielectric is its ability to support an electrostatic field while dissipating minimum energy in the form of heat. The lower the dielectric loss of a material the more effective is that dielectric material. Another thing which comes into consideration is the dielectric constant which describes the extent to which a substance concentrates the electrostatic lines of flux. Some of the substances having a low dielectric constant are perfect vacuum, dry air, and most pure and dry gases such as helium and nitrogen. Materials having moderate dielectric constants include ceramics, distilled water, glass etc Metal oxides mostly have high dielectric constants.

1.1.3 Polarization of Dielectrics

Dielectrics is subdivided into two groups :

1) Non-Polar dielectrics which behave as an insulator

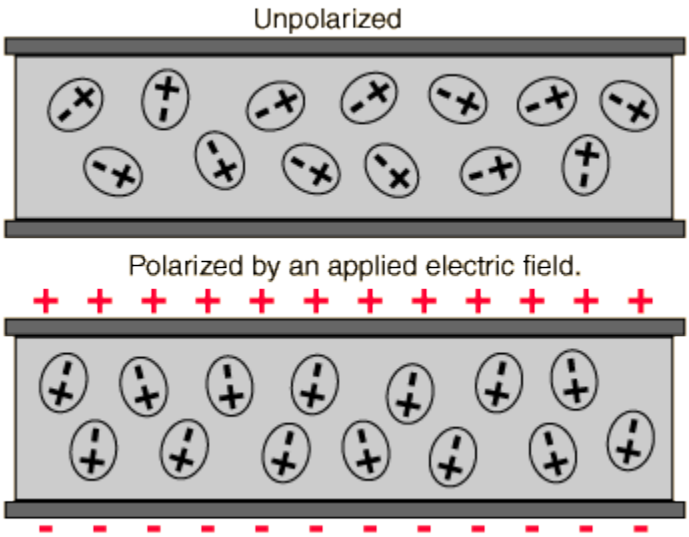
2) Polar dielectrics are the dielectrics in which the molecules or atoms possess a permanent dipole moment which is ordinarily randomly oriented and becomes more or less oriented by the application of an external electric field.

If a material contains polar materials, they will be in random orientations but without any electric field. On applying electric field it will be polarized. This will cause increase in the capacitance of the parallel plate structure.

The presence of any dielectric material decreases the electric field produced by a given charge density [2].

$E_{effective}=E-E_{polarization}=\sigma/k\varepsilon_0$

Here k= dielectric constant of the material



1.1.4 Calcium Copper Titanate (CCTO)

Calcium copper titanate, $CaCu_3Ti_4O_{12}$ (CCTO) is a perovskite structure that has a body-centered cubic crystal structure with slightly tilted [TiO_6] octahedra facing each other [3, 4]. CCTO ceramics exhibit ferroelectric (FE) hysteresis loops, despite the fact that it belongs to the centrosymmetric space group, and remnant polarization and coercive field values were found to be strongly dependent on the sintering conditions. This material shows a huge dielectric constant(ε_r) sometimes larger than 50×10^3, over a wide temperature range, i.e. from 100 to 400K [3]. Due to high ε_r, elaborative investigations are done on this topic such as the influence of the microstructure, electrode material and pellet thickness on impedance and dielectric characteristics. CCTO is also utilized to manufacture many of the electronic components such as multilayer capacitor, electronic devices in automobiles and aircrafts. They can also be applied to important devices such as DRAM (Dynamic Random Access Memory), microwave devices and

many more. Since CCTO structure is derived from the cubic perovskite by an octahedral tilt distortion, this is caused due to the size mismatch and the nature of the A cations. The TiO_6 octahedra tilt to produce a structure where three-quarters of the A sites have square–planar coordination and are occupied by Jahn–Teller Cu^{2+} ions. The remaining quarters of the sites is occupied by Calcium [5].

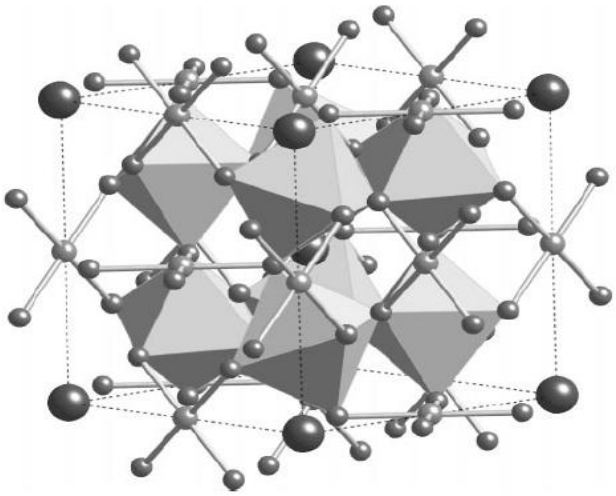


Fig 1.1.4.1 The structure of $CaCu_3Ti_4O_{12}$ shown as TiO_6 octahedra where Cu atoms are bonded to four oxygen atoms and large Ca atoms without any bond

1.1.5 Importance of CCTO ceramics

The interesting feature observed in CCTO ceramics is the existence of a nonlinear current–voltage characteristic [6, 7]. This non-Ohmic behavior was considered to be due to Schottky-type electrostatic barriers at the grain boundaries [6, 8]. These results seem to support the idea of an extrinsic origin for the ultrahigh dielectric properties [9]. All these large dielectric constant materials have similar dielectric behavior, i.e., they all exhibit a Debye-like relaxation and their dielectric constants are nearly independent of frequency and temperature well below the relaxation frequency. Usually large dielectric constants are found in ferroelectric materials.

CCTO is non-ferroelectric and has no structural changes down to 35 K. The dielectric properties make CCTO a desirable material for micro-electric applications such as static and dynamic random access memories and thin film devices. This material exhibits no crystallographic structural phase transition, associated with spontaneous polarization. The ultra-miniaturization of electronic devices in automobiles and aircraft requires the development of high dielectric materials that should be stable over a wide range of temperatures. Research indicates that $CaCu_3Ti_4O_{12}$ may be part of a new class of oxide perovskite whose high dielectric properties are different than classic ferroelectrics or relaxors. Diffraction experiments detect no presence of superstructure peaks or diffuse scattering or broadening in Bragg intensities which are often indicative of nanodomains or disorder effects that are associated with relaxors.

1.1.6 Colossal Dielectric Constant in CCTO

The colossal dielectric constant (CDC) phenomenon, which was firstly observed in $CaCu_3Ti_4O_{12}$(CCTO) ceramics through intensive investigations which were conducted in both experimental and theoretical ways at bulk ceramics, single crystals [10,11] and polycrystalline as well as epitaxial thin films on various substrates [12,14]. All of these samples showed the characteristic CDC features. In the year 2002, D.Sinclair et al. concluded from impedance spectroscopy that CCTO ceramics is electrically heterogeneous which composed of semiconducting grains having insulating grain boundaries, and attributes the CDC phenomenon to an internal barrier layer capacitance (IBLC) [13]. This explanation proved to be correct for the ceramic CCTO case, but formed difficulties when it was applied to the single crystals, nevertheless show the CDC phenomenon [10]. The IBLC model is supported by the fact that CCTO grains are semiconducting [10, 11]. However, the contradictive fact is that the CCTO optical band gap of 2.5eV predicted a good dielectric material below the room temperature. *I-V*

and *C-V* measurements indicated that Schottky barriers or metal–insulator–semiconductor (MIS) junctions were formed at the thin film top electrode interfaces [12]. By annealing at an intermediate temperature in air, the CDC state can be converted to a non-CDC state, where we able to observe the intrinsic dielectric properties of the sample. The XPS profiles of the CDC and non-CDC states showed that they corresponded to low and high Cu oxidization states respectively [10]**.** In order to account for the semi-conductivity in CCTO, two models have been proposed so far. First, it is known that TiO_2-based perovskite ceramics such as $BaTiO_3$ and $SrTiO_3$ become more conductive during sintering under reducing conditions due to a small amount of oxygen loss occurring at high temperatures. On the other hand, a cationic non-stochiometric model was suggested. With the recent report that a Cu_2O phase was observed inside a decomposition zone with a negligible change in bulk resistivity during nitrogen or oxygen annealing, the semiconducting behavior in CCTO is due to non-stoichiometric model.

1.1.7 Dielectric properties of CCTO

We found that the perovskite-related body-centered cubic materials $CaCu_3Ti_4O_{12}$ (CCTO) exhibited in giant dielectric constant at room temperature and also the dielectric constant between 100 and 400 K. These properties are very important for device implementation and microelectronic application but its nature and characteristics remain unsolved. From the structural studies we found that CCTO maintains a cubic structure without phase transitions.

CHAPTER-2

LITERATURE REVIEW

2.1 Different Modes of Synthesis of CCTO

There are different synthesis processes for the preparation of CCTO

- Solid state synthesis
- Sol-gel method
- Pulsed laser deposition
- Chemical layer deposition
- Precursor oxalate route

1) X. H. Zheng *et al*. [15] prepared CCTO ceramics by the conventional solid-state reaction method. The sample was characterized by XRD, SEM, and dielectric measurement. $CaCu_3Ti_4O_{12}$ (CCTO) ceramics were sintered with different temperatures or durations. To appropriately extend sintering time would benefit the densification and formation of bigger and uniform grain of CCTO ceramics. The samples sintered at 1120 ℃ for 3 h showed the lowest permittivity of about 514 at 1 kHz, and the ones sintered at 1120 ℃ for 6 h gave the highest value larger than 12,400. Furthermore, the larger grains resulted in higher permittivity.

2)Julie J. Mohamed *et al.* [16] synthesized CaCu3Ti4O12 by the solid state reaction route. The sample was calcined at 900oC for 12 hrs and sintered at 1050℃ for 24 hrs. The increase in sintering temperature found to improve the density and secondary phase formation of Cu_2O. A clear grain boundary and a dense microstructure were seen in the sintered samples. We came to know that the sample sintered at 1040℃ for 10 hrs yielded a uniform grain size with the highest ε_r.

3) B.A.Bender *et al*. [17] prepared $CaCu_3Ti_4O_{12}$ using conventional ceramic solid state reaction processing techniques. The standard sintering conditions were considered to be 1100 ^oC for 3 h. XRD was used to monitor phase evolution for the various mixed powders and resultant discs. Microstructural characterization was done on the fracture surfaces using scanning electron microscopy (SEM). The capacitance and dielectric loss of each sample were measured as a function of temperature (−50 to 100 ^oC) and frequency (100 Hz to 100 kHz) using an integrated, computer controlled system. The dielectric properties of a standard processed sample (AM2) was also measured as a function of dc bias using a high voltage power supply in combination with a blocking circuit to protect the LCR meter (Hewlett-Packard 4284A) from the dc bias voltage.

2.2 Objective

The objectives of the project are

1) To prepare CCTO by conventional solid state reaction route.

2) To optimize the synthesis process to obtain high density CCTO ceramics.

3) To obtain high dielectric constant for capacitor application.

2.3 Experimental procedure

CCTO was synthesized by conventional solid state reaction route.

$$CaO + 3CuO + 4TiO_2 \rightarrow CaCu_3Ti_4O_{12}$$

Steps involved for the synthesis of this compound are given below:

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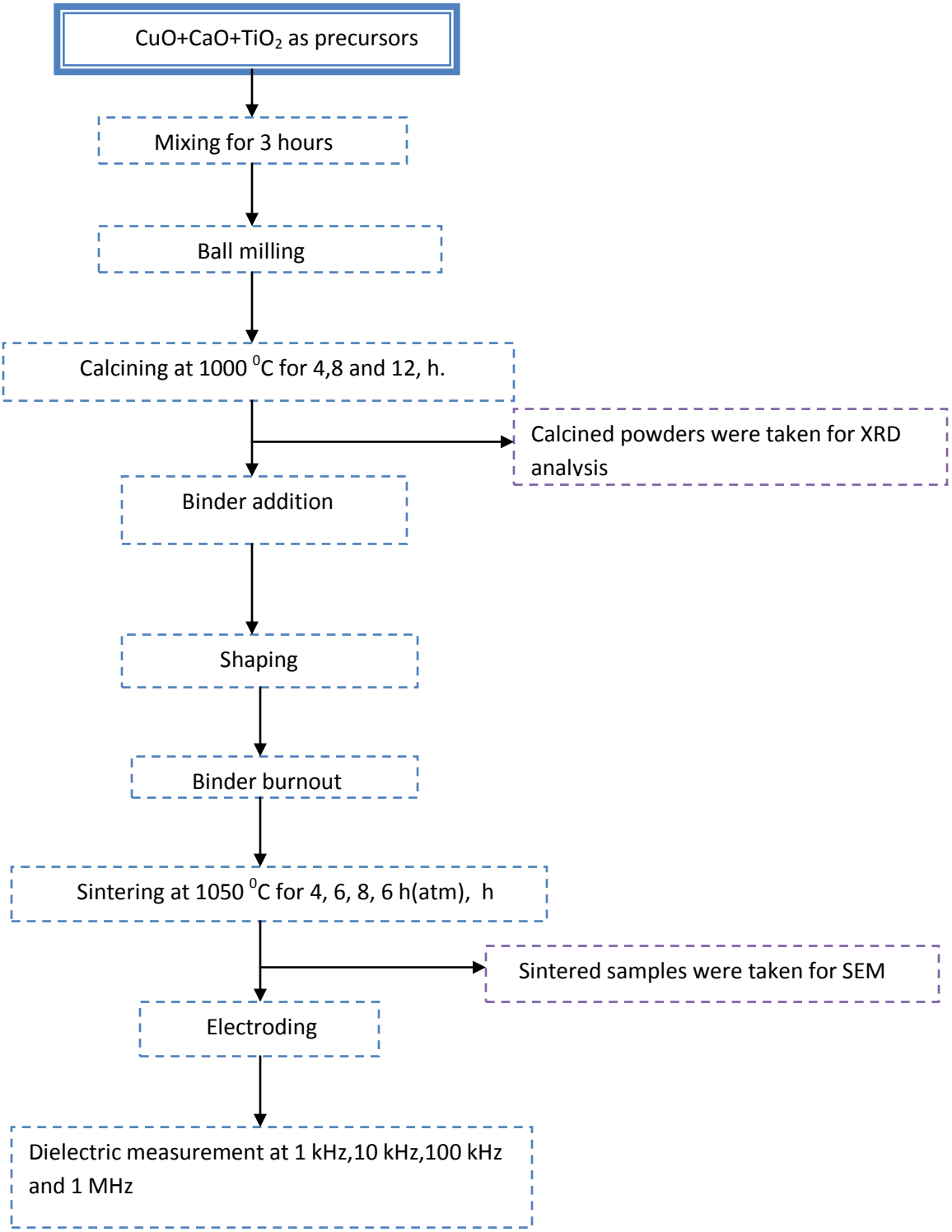
1) CaO (calcium oxide), CuO (copper oxide) and TiO_2 (titanium dioxide) were taken in stoichiometric ratio to prepare $CaCu_3Ti_4O_{12}$. The raw materials were measured using the high precision balance correct up to 4 decimal places and

were together ball milled for 6 hours using zirconia balls (powder to balls ratio 1:3) and acetone as grinding medium.

2) The mixed sample was taken out and after it got dry it was thoroughly grounded in agate mortar for nearly 1 hour so as to obtain a mixed powder of the raw materials.
3) The grounded sample was taken in an alumina crucible and calcined at 1000 °C for 12 hours, 8 hours and 4 hours followed by furnace cooling.
4) The mixtures were taken out after the temperature came down to room temperature.
5) The TGA and DSC of the calcined powder was done.
6) Phase formation of CCTO was confirmed through X-ray diffraction analysis using powder diffractometer (PHILIPS, PW 3020)
7) Single perovskite phase was confirmed from XRD analysis for the sample calcined for 12 h.
8) The calcined sample at 1000 ^{0}C for 12 h was chosen and mixed with polyvinyl alcohol that acts as a binder. After mixing the binder the sample is left for sometime so that the mixture dries and then grinded again.
9) For sintering the powdered sample was pressed in the form of cylindrical pellets of 0.5 grams each. The Pelletization involves the uniaxial pressing using rigid dies with a pressure of 60 MPa.
10) The CCTO pellets were sintered in an indigenous programmable conventional furnace at 1050 ^{o}C for 4, 6 and 8, h, respectively in normal atmosphere and 6 h in oxygen atmosphere.

10) The grain size in the sintered pellets was studied by SEM.

11) The sintered pellets were coated with silver paste and heated for 5-10 minutes to dry the coating and for good adhesion. The dielectric measurement was then made at 1kHz, 10kHz, 100kHz and 1MHz and also at atmospheric condition.



2.4 Calculations

1) For starting powders

$$CaO + 3CuO + 4TiO_2 = CaCu_3Ti_4O_{12}$$

For the preparation of 15 grams of $CaCu_3Ti_4O_{12}$, the amounts of the raw materials used are as follows:

SAMPLE USED	MOLECULAR WEIGHT	QUANTITY
a) CaO	56.0774 g/mol	1.3692 grams
b) CuO	79.545 g/mol	5.8268 grams
c) TiO_2	79.9 g/mol	7.8038 grams

These raw materials was first mixed thoroughly using ball milling technique and then grinded in the agate mortar for nearly 1 hour so as to form a fine mixture of the mixed powders. The powder obtained after grinding was grayish in appearance which changed to dark brown after calcination.

2.5 Calcination

After synthesis the powdered sample is calcined in a tubular furnace for 4 hours, 8 hours and 12 hours at 1000°C temperatures at a heating rate of 5 °C per minute. The furnace takes nearly 4 hours and some minutes to reach the desired temperature after which the sample was calcined at the desired temperature for 4 hours, 8 hours and 12 hours. Then the furnace was cooled and the sample was thoroughly grinded to ensure that there are no agglomerates in the sample.The

calcination temperature are affected by the electrical and mechanical properties of the ceramics to a large extent. At the high calcination temperature the homogeneity and the density of the resultant ceramic will also be high. So, the calcination temperature is to be taken carefully.

2.6 Binder addition

The calcined sample at 1200 ^{0}C was chosen and mixed with polyvinyl alcohol that acts as a binder. The binder helps in increasing mechanical strength of the pellets that are to be formed for sintering.

2.7 Shaping

After binder addition the CCTO powder was converted to cylindrical shaped pellet of 0.5gm of thickness by the method of pressing of powder which includes die pressing.

2.8 Binder burnout

After the formation of the pallets they were heated very slowly upto 600 ^{0}C at a rate of 2 ^{0}C/min in order to allow the gases to come out slowly without forming any cracks.

2. 9 Sintering

The pellets were then sintered in a conventional furnace at 1050 ^{0}C for 4, 6 ,8 hours and for 6 hours in the presence of oxygen with a heating rate of 5 ^{0}C per minute. In the sintering stage the shaped powder form is heated to produce the desired microstructure which leads to the densification of the body occurred by atomic diffusion.

2.10 Electroding

The sintered pellets were coated with silver paste and heated for 1 hour at 170 ^{0}C in the muffle furnace. The coating should be very thin having a good physical and chemical durability.

CHAPTER 3

3.1 Characterization Techniques

3.1.1 Principle of DSC and TGA experiment

The schematic principle of the TGA measurement is shown in Fig 3.1.1.1. The sample is heated under nitrogen or synthetic air in a constant heat rate while in between the difference of the mass is measured. The loss in mass indicates that the substance degrades. The increase of mass is due to reaction with oxygen from the synthetic air.

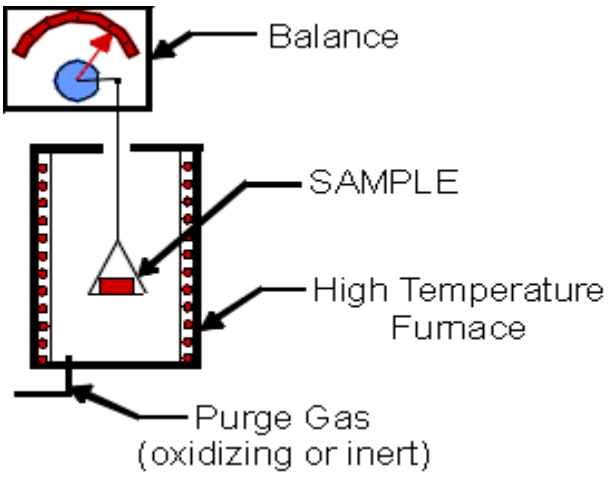


Fig.3.1.1.1 TGA measurement Apparatus

The DSC can be used to obtain the thermal critical points. Some of them are melting point, the enthalpy specific heat or the glass transition temperature of substances. The principle of the DSC is described in the figure2. The sample and an empty reference crucible are heated at a constant rate. A difference of the temperature of both crucibles comes into picture. This is caused by the thermal critical points of the sample and hence can be detected.

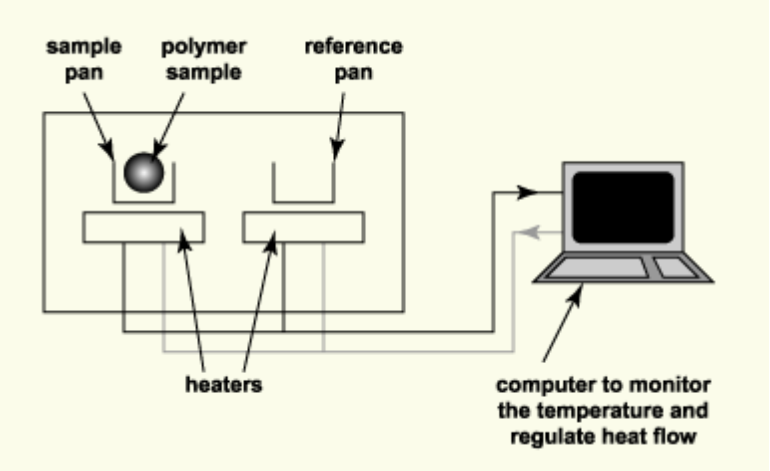


Fig 3.1.1.2: DSC measurement apparatus

3.1.2 Principles of X-ray Diffraction

X-ray diffraction is based on the interference of monochromatic X-rays and a crystalline sample. It is used for determining the arrangement of atoms within a crystal .In diffraction process a beam of x-rays strikes a crystal and causes beam to spread into many specific directions. These X-rays are generated by the help of a cathode ray tube. These x-rays are collimated to concentrate, and are directed towards the sample. A pictorial presentation of this arrangement is shown in Fig.3.1.2.1

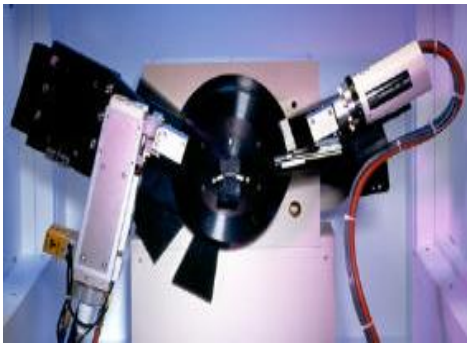


Fig. 3.1.2.1: Photograph of an x-ray source, sample holder and detector in a diffraction arrangement.

The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda=2d \sin\theta$).

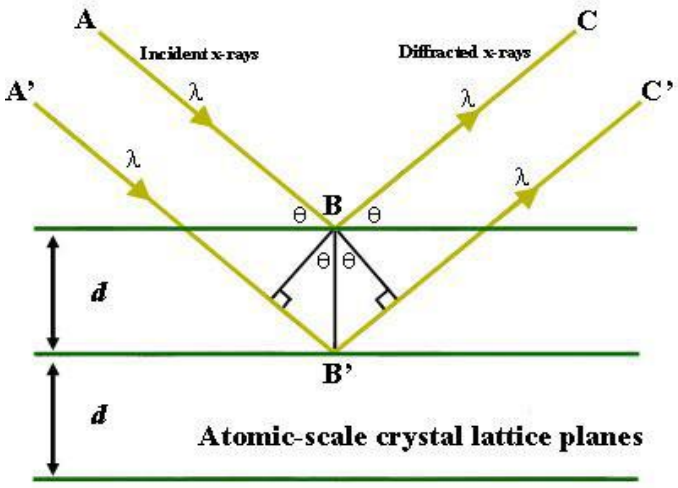


Fig3.1.2.2: Bragg's law of X-ray diffraction

By scanning the sample all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material.. The X-rays are directed towards the sample, and their corresponding diffracted rays are collected. The angle between the incident and diffracted rays helps in diffraction. Accordingly, phenomena like constructive and destructive interference should become observable when crystalline and molecular structures are exposed to x-rays.

In the X-ray diffraction methods, the scattering is elastic i.e. the scattered X-rays have the same wavelength as the incoming X-ray. In X-ray diffraction work we normally distinguish between single crystal and polycrystalline or powder applications. The single crystal sample is a perfect (all unit cells aligned in a perfect extended pattern) crystal with a cross section of about 0.3 mm. In powder or polycrystalline diffraction sample is having a smooth plane surface. To have a smooth and flat surface the sample is pressed into a sample holder.

The intensity of the reflected x-rays is recorded by rotating the sample and the detector. In the present work XRD was done using Philips analytical XRD machine with the wavelength of K-radiation = 1.5418 Å.

3.1.3 XRD-Analysis

XRD patterns were obtained using an automated diffractometer. It was diffracted for 22 min at 20-70° The XRD pattern obtained were compared with the available XRD pattern of CCTO which was found to be in accordance with the available CCTO XRD pattern.

3.1.4 Principles of Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. In the sample the electrons interact with electrons and produces signals that can be detected and gives information about the sample's surface topography and its composition. The beam of the electron is scanned in a scan pattern named as raster scan. Here the beam's position is combined with the detected signal to produce an effective image. Resolution better than 1 nanometer can be achieved through SEM.

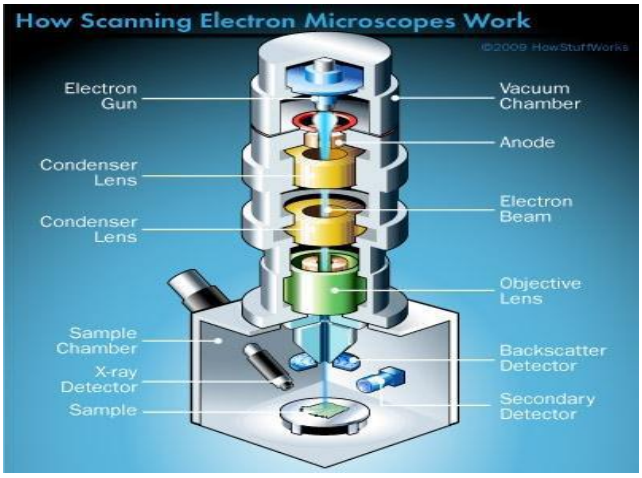


Fig 3.1.4.1: A schematic diagram of SEM

3.1.5 Dielectric measurement

Dielectric constant and its loss were calculated by electroding the samples with a conducting paste named as silver paste. Then these samples were heated at 780^0C so as to dry the paste on the pellets completely. Using the computer interfaced HIOKI 3532-50 LCR-HITSTER the dielectric measurement was done. The data was collected for dielectric constant (ε_r) and dielectric loss (tan δ) upto 400^0C temperature as well as at room temperature. The frequency range set was from 1 kHz to 1 MHz.

The capacitance of a dielectric material can be calculated as follows:-

$$\mathbf{C = K\ \varepsilon_0\ A\ /d}$$

Where C = Capacitance

K=dielectric constant of the material

A= area enclosed by the electrode

ε_0 = permittivity of the free space

CHAPTER 4

RESULTS AND DISCUSSION

4.1.1 TGA and DSC

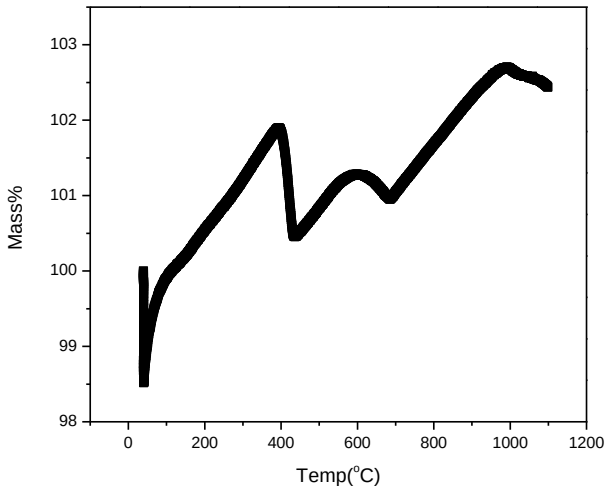


FIG 4.1.1.1: TGA Analysis

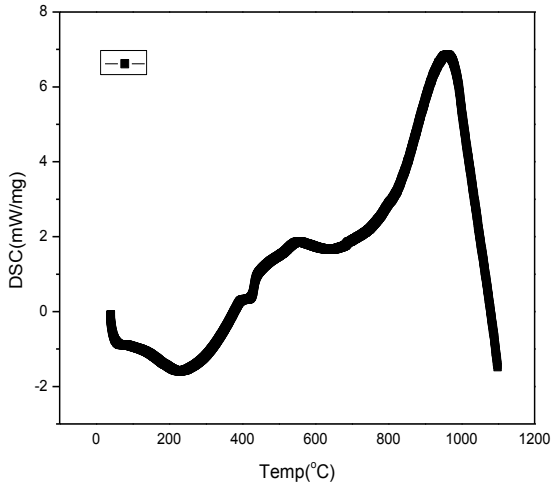


FIG 4.1.1.2: DSC Analysis

The TGA curve shows the increase in mass % of the sample with increase in the temperature. From this we can easily conclude that the mass reacts with oxygen in the ambient air. As the sample undergoes exothermic processes a very less amount of heat is required to raise the sample temperature. In the present experiment by absorbing a small amount of heat a sharp peak was observed in 1100^0C, which confirmed that the sample undergoes exothermic reaction.

4.1.2 Structure analysis from XRD peaks

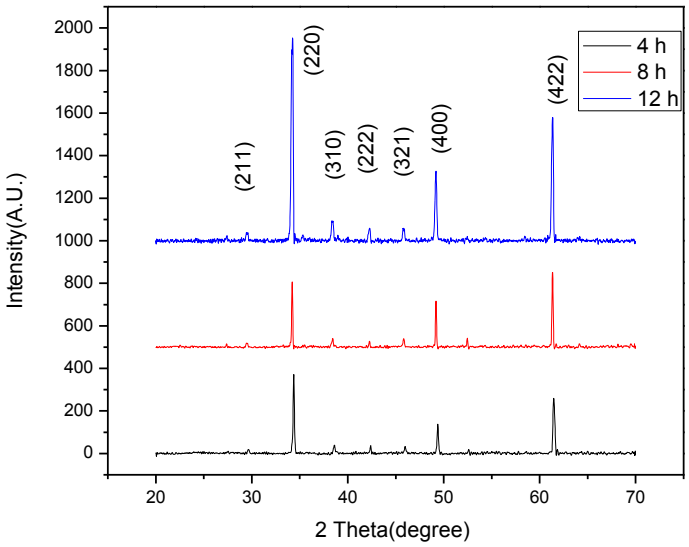


Fig 4.1.2.1: XRD peaks

Fig. 4.1.2.1 shows the XRD patterns of the CCTO calcined at 1000 ^{0}C for 4, 8 and 12, h respectively. The XRD patterns confirm the single phase ABO_3 structure. At the composition we a get sharp peaks in the 2θ range at 29.57°, 34.45°,38.47°,49.38° and 61.45°. Small peaks can also be seen around 38.47°, 49.38° and 61.45° respectively. Some impurities can also be detected around at some places. At 1000 °C the maximum peak is achieved at 34.45°. The peaks are

indexed as per the (hkl) values reported in the JCPDS file. Appearance of the peaks corresponding to the CCTO phases indicated formation of single phase compound.

4.1.3 Density measurements

Densities of $CaCu_3Ti_4O_{12}$ sample were measured. The values are as shown in the given table

Table 1: Density measurement of the CCTO ceramic samples

Sample sintered in different temperatures	Dry weight (gm)	Soaked weight (gm)	Density(gm/cm^3)
4 hours	0.3982	0.3101	4.5199
6 hours	0.4035	0.3198	4.8208
6hours(atmospheric)	0.1298	0.0973	3.9938
8 hours	0.3223	0.2528	4.6374

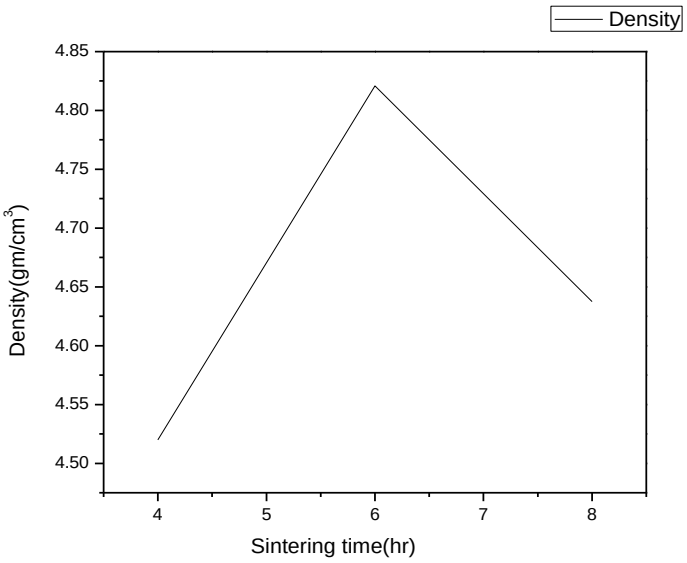


Fig. 4.1.3.1 Variation of density with sintering time

The highest density was obtained to be 4.8208 g/cm^3. The density in conventional method was found to be highest for the sample sintered at 1050^{0}C for 6 hours followed by the samples sintered for 4, 6 (atmospheric) and 8, h respectively.

4.1.4 Scanning Electron Microscope

The SEM images for CCTO samples were taken and their grain sizes were calculated.

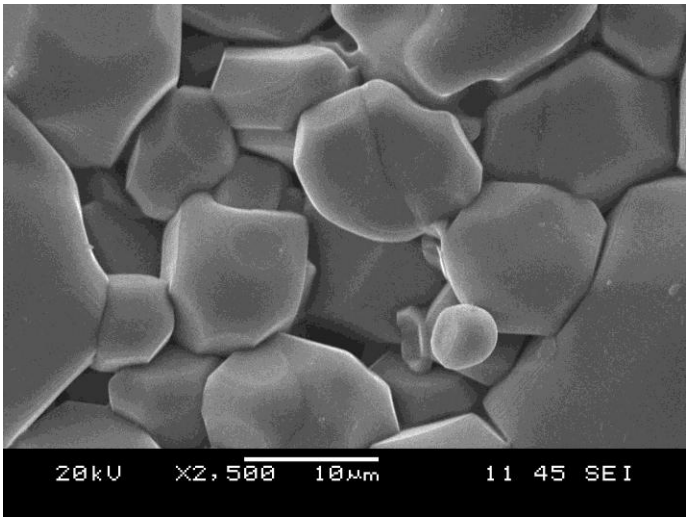


Fig 4.1.4.1: SEM of sample Sintered for 4 hours at 1050 ^{o}C

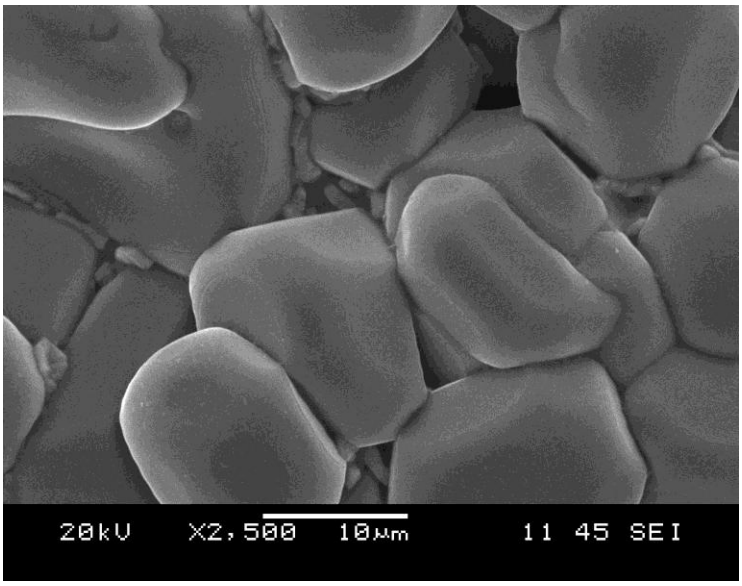


Fig 4.1.4.2: SEM of sample Sintered for 6 hours at 1050 ^{o}C

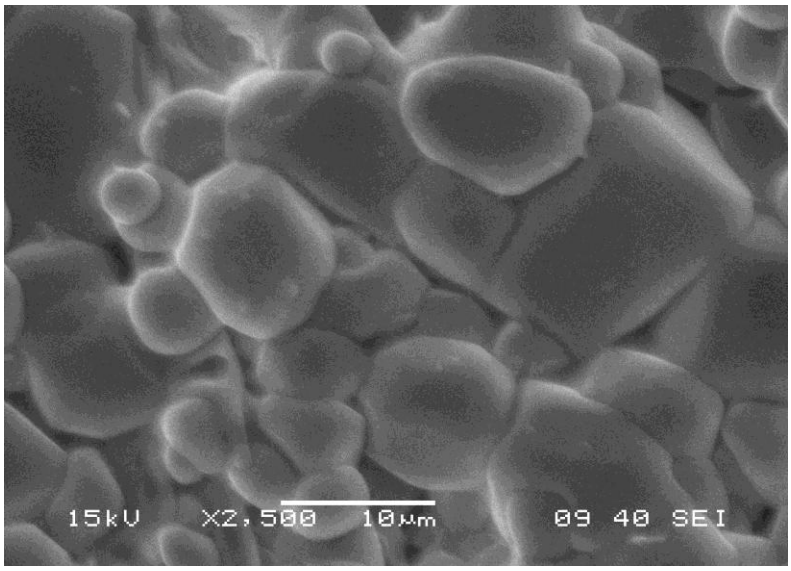


Fig 4.1.4.3: SEM of sample Sintered for 6 hours in the presence of oxygen

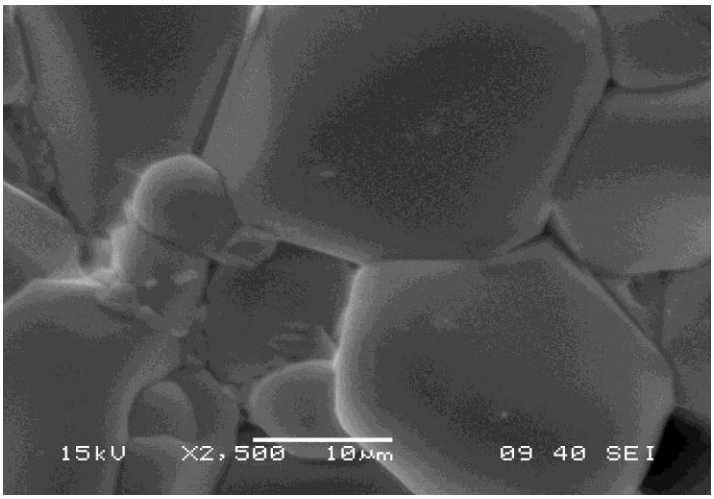


Fig 4.1.4.4: SEM of sample Sintered for 8 hours at 1050 ^{o}C

From these images the grain sizes were calculated which are listed in the table below.

Table 2 Grain size of the CCTO ceramic samples

Sintering time	**Grain size in µm**
4 hours	~7.725
6 hours	~9.5
6 hours(atmospheric)	~5.5
8 hours	~10

From the Table 2, it can be observed that with the increasing temperature, the grain size increases due to atomic diffusion but the sample sintered in the presence of oxygen for 6 hours

has lesser density as compared to the sample sintered in the furnace for 6 hours. So this concludes that sintering in the presence of oxygen reduces the growth of the grain size.

4.1.5 Dielectric Measurements:

Dielectric constant & tangent loss vs. frequency is for all the $CaCu_3Ti_4O_{12}$ samples measured by HIOKI LCR 3532-50 Hi Tester were as shown below:

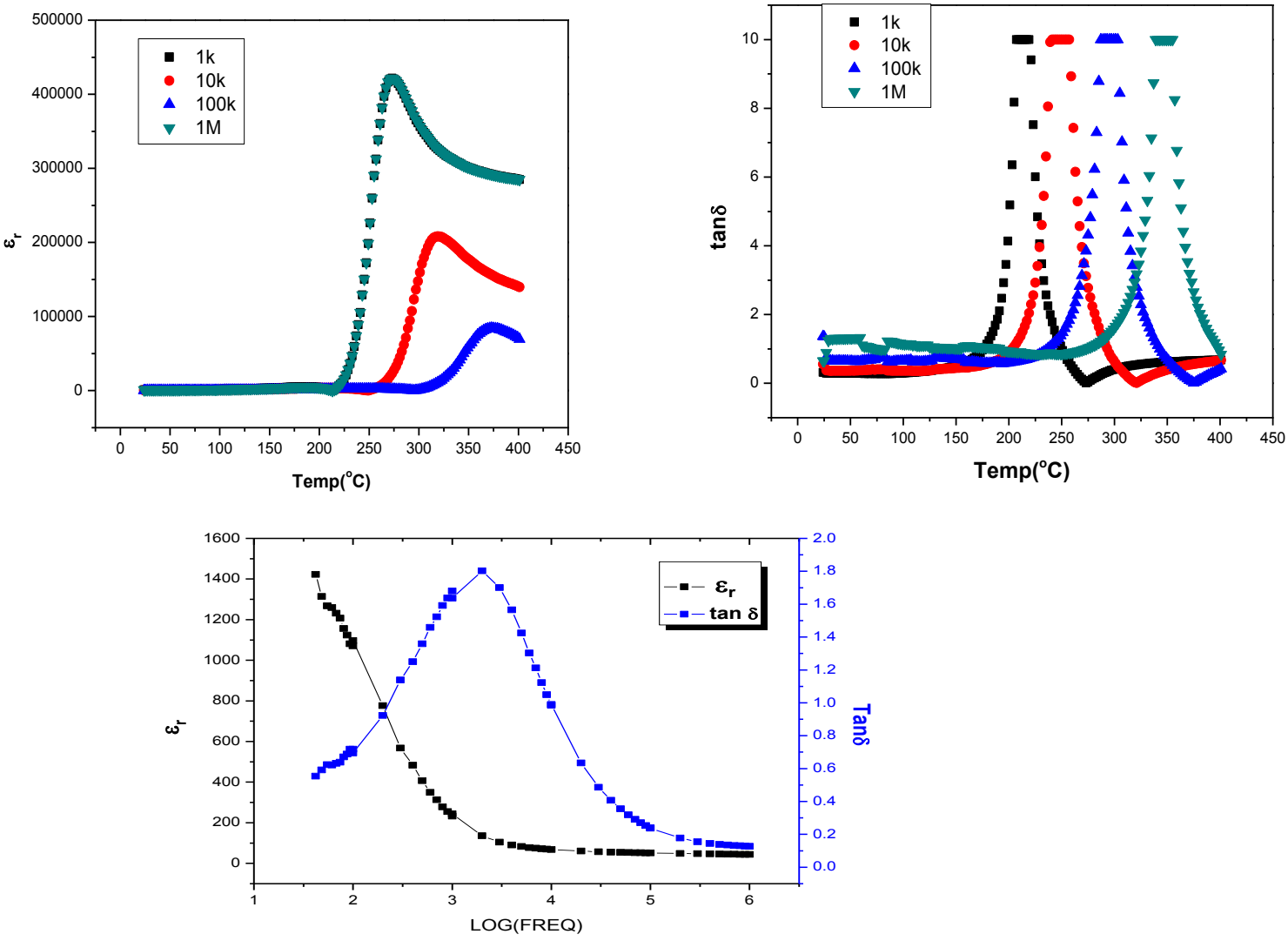


Fig.4.1.5.1. Variation of (a) dielectric constant and (b) dielectric loss with temperature and (c) dielectric constant at room temperature for sample sintered at 1050°C for 4 hours

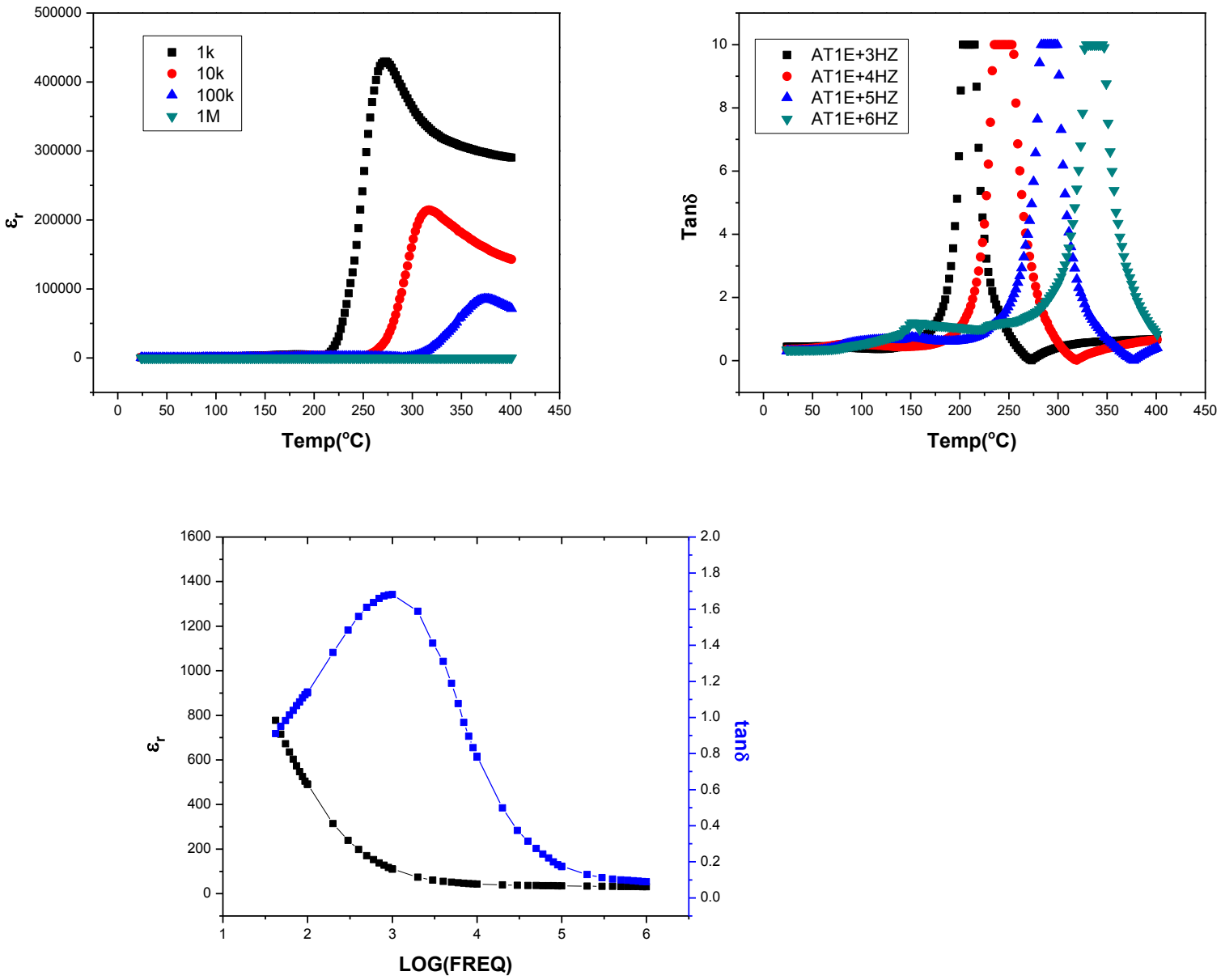
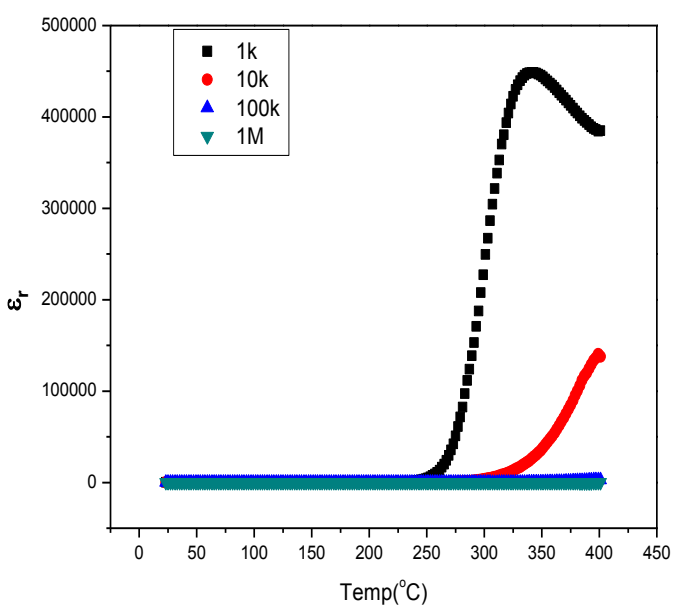
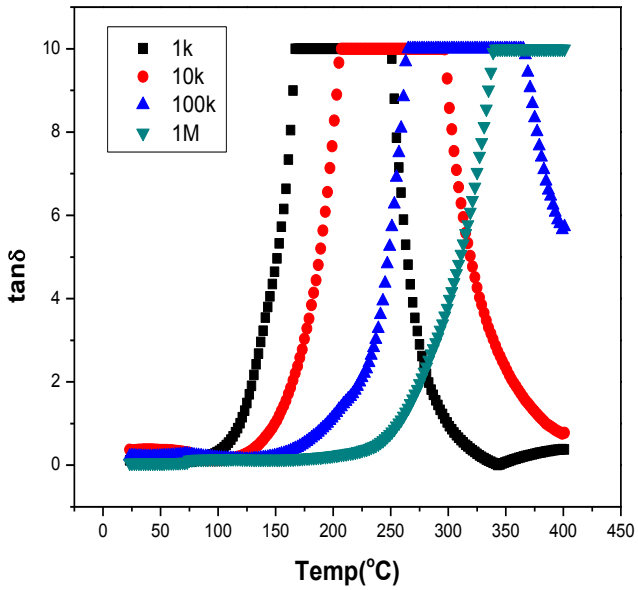


Fig. 4.1.5.2. Variation of (a) dielectric constant and (b) dielectric loss with temperature and (c) dielectic constant at room temperature for sample sintered at 1050^{o}C for 6 hours





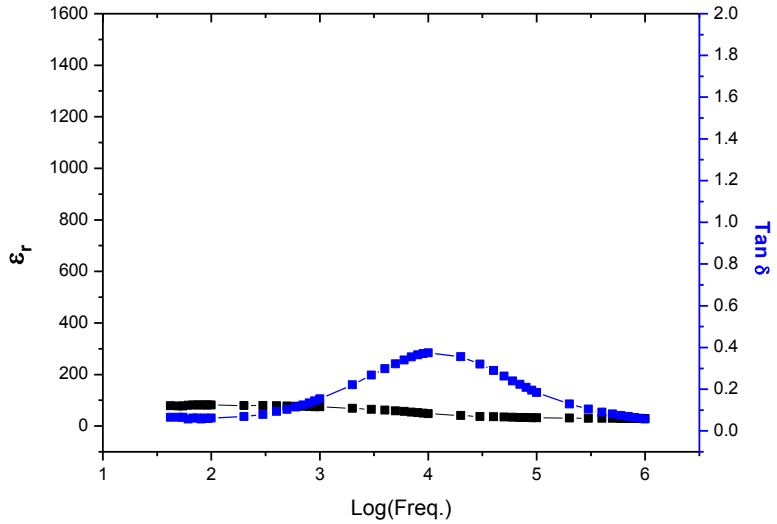


Fig.4.1.5.3. Variation of (a) dielectric constant (b) dielectric loss with temperature and (c) dielectric constant at room temperature for sample sintered at 1050 ^{0}C for 6 hours (oxygen atmospheric condition)

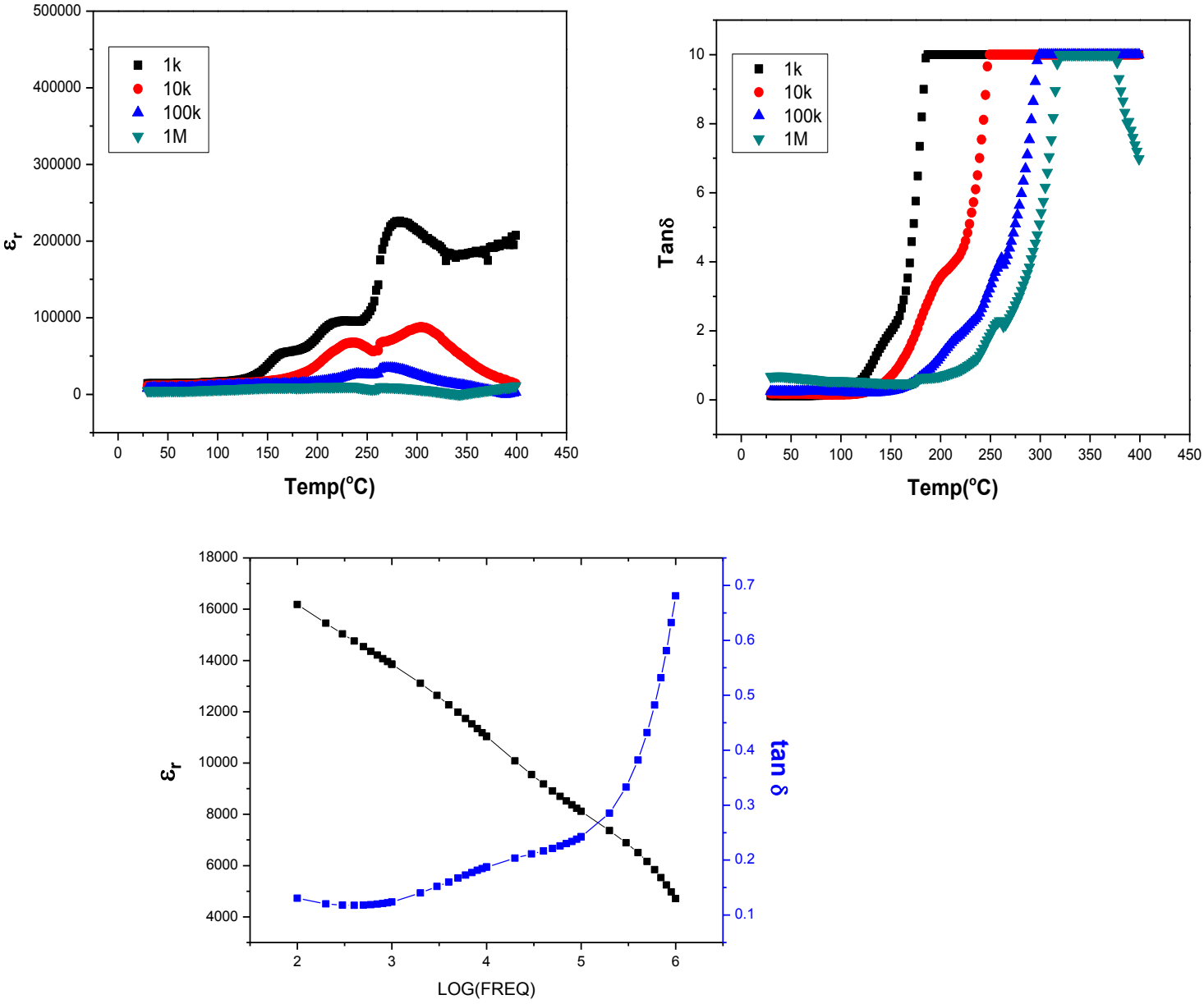


Fig.4.1.5.4. Variation of (a) dielectric constant and (b) dielectric loss with temperature and (c) dielectric constant at room temperature for sample sintered at 1050 ^{0}C for 8 hours

The value of dielectric constant increases with increase in temperature due to increase in polarization because of separation of negative and positive charges at higher temperature. This process is called as displacive transition. After attaining the critical temperature, it starts

decreasing with further increase in temperature which indicates a phase transition to paraelectric from ferroelectric phase.

CONCLUSIONS

The Calcium Copper Titanate (CCTO) is successfully synthesized by solid state reaction route. XRD peaks reveal the formation of single phase perovskite structure for the composition. The SEM micrographs showed the dense microstructures for CCTO ceramics sintered at different temperatures. The growth of grain size for CCTO at atmospheric condition is lower as compared to that of CCTO sintered at 6 hrs ceramics. The bulk density increased with increasing sintering temperature of the ceramics. Density was highest for the sample sintered at 1050 ^{o}C for 6 hrs. The dielectric study was carried out for the samples and the sample sintered for 6 hrs in the atmospheric condition has the highest relative permittivity (ε_r) in 1 kHz frequency.

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